

PATENT SPECIFICATION

NO DRAWINGS

1.191.983



1.191.983

Date of Application and filing Complete Specification: 25 Feb., 1969.
No. 10118/69.

Application made in Italy (No. 831996) on 11 April, 1968.

Complete Specification Published: 13 May, 1970.

Index at acceptance: —C2 C(B4B, B4H)

International Classification: —C 07 d 1/14

COMPLETE SPECIFICATION

Preparation of Ethylene Oxide

We, SOCIETA' ITALIANA RESINE S.P.A., an Italian Joint Stock Company, of 33 Via Grazioli, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of ethylene oxide by the catalytic oxidation of ethylene.

Ethylene oxide is a very important product as an intermediate for a number of commercial syntheses, particularly of ethylene and polyethylene glycols, glycol ethers, ethan-
olamine, acrylonitrile and surfactants.

It is known to produce ethylene oxide by the catalytic oxidation in the vapor phase of ethylene with oxygen-containing gases, generally by reacting ethylene with oxygen, both diluted with inert gases, at high temperatures and pressures, in the presence of an active silver catalyst. Suitable diluents include nitrogen, helium, argon and carbon dioxide.

Nitrogen is almost exclusively used in actual practice. Thus, oxidation of ethylene is carried out by employing oxygen-nitrogen mixtures, preferably air. The unreacted gases may be recycled to the reactor, but the extent of this recycle is limited by the necessity of removing excess nitrogen, which would continuously increase by the addition of air to the oxidation reactor. Consequently, an appreciable portion of the unreacted gases is lost with the nitrogen. In order to limit the loss of ethylene thereby, the withdrawn gases are mixed with air and passed through one or more additional oxidation reactors in the presence of the silver catalyst under rather drastic conditions. However, this appreciably increases the manufacturing costs.

Moreover, although these known processes have a fairly good selectivity in the conver-

sion of ethylene they have an unsatisfactory rate of conversion. In other words, the rate of conversion of ethylene to the reaction products on each flow over the catalyst is rather low.

It is therefore an object of this invention to provide a method of manufacturing ethylene oxide which avoids the aforesaid difficulties.

It has now been found in accordance with this invention that ethylene oxide may be obtained by the catalytic oxidation in the vapor phase of ethylene, by supplying to the oxidation reactor substantially pure ethylene and oxygen, separately or mixed together, without dilution with other gases, the ethylene constituting more than 86% by volume with respect to the inlet gases to the oxidation reactor.

According to the process of the invention, ethylene and oxygen, separately or premixed, the ethylene constituting over 86% by volume of the total gaseous charge, the remainder being essentially oxygen, preferably 4 to 6% by volume, is fed to a reactor over an oxidation catalyst at high temperature and a pressure of 1 to 30 atm.

The outlet gases from the oxidation reactor are, in a preferred embodiment, treated and recycled as follows. The gases are suitably cooled and conveyed through a first scrubbing column, in which the ethylene oxide is separated. The gases issuing from the first column are conveyed through a second scrubbing column, in which the carbon dioxide and any other by-products of the oxidation reaction are separated. Fresh oxygen and ethylene are added to the gaseous mixture issuing from the second tower, to bring it to its original composition (>86% ethylene) and the mixture is recycled to the oxidation reactor.

The catalyst used in the reactor is pre-

[Price 5s. 0d.]

BEST AVAILABLE COPY

1.191.983-1 (USPTO)

ferably relatively non-porous silver deposited on an inert carrier. The carrier should have a high heat conductivity so as to dissipate the heat of the reaction; suitable carriers are aluminium oxide, silicon carbide and beryllium oxide. An alkali or alkaline earth metal salt may be incorporated as a promoter. The silver should constitute 5 to 20%, most preferably 13 to 15%, by weight of the catalyst. The catalyst is preferably used in the form of a stationary bed.

The reaction is preferably carried out at a temperature of 150° to 450°C, most preferably 250° to 320°C, and 10 to 20 atm.

The gaseous reactants may be commercial ethylene of >99% purity (the remainder being methane and ethane), and oxygen of at least 95% or preferably >99% purity.

The residence time of the mixture in the oxidation reactor should be 3 to 10 seconds, preferably 5 to 8 seconds.

The ethylene oxide is separated from the gaseous reaction mixture by selective absorption into a suitable solvent, such as water, and subsequent stripping of the resulting solution. This may be done by cooling (e.g. in a heat exchanger) the gas issuing from the oxidation reactor to a temperature below about 130°C, and then passing it to the bottom of an absorption column (or scrubber) wherein it travels upwards, countercurrently to water or other solvent percolating from the top. The absorption column is preferably maintained at a pressure of from 1 to 30 atm and a temperature of 5 to 80°C, most preferably 20 to 40°C. The water is desirably supplied in such quantity that the resulting solutions contain 1 to 3 weight % of ethylene oxide.

The gas from which ethylene oxide has been separated should be purified from carbon dioxide before being recycled to the oxidation reactor. The gas may be supplied to the bottom of a second absorption column wherein it flows countercurrently to a suitable absorbing solution. Aqueous solutions of ethanolamine, diethanolamine, sodium hydroxide, or alkali carbonates may be used for the purpose.

The thus purified gas is restored to its original composition by addition of fresh oxygen and ethylene, and is again passed through the oxidation reactor.

As compared with the prior art, the process of the invention yields ethylene oxide with high selectivity in conversion of ethylene, even at high conversion rates. Selectivities with respect to ethylene exceeding 70% are obtained by conversions per pass with respect to oxygen exceeding 50%. Overall conversions in respect of ethylene reach very high values, mostly exceeding 95%. The result is a considerable improvement in the rate of production of ethylene oxide.

By the absence of inert diluents the process

of the invention avoids the use of additional oxidation reactors, whereby the apparatus and operation are considerably simplified. Finally, the absorbed carbon dioxide may be recovered by the process of the invention in a practically pure form and in a substantially complete manner, and may be directly utilized for any desired purpose.

The following Examples illustrate the invention.

EXAMPLE 1

A gaseous mixture of the volumetric composition: ethylene (99.7% purity) 90.5% by volume; oxygen (99.5% purity) 9.5% by volume was passed through an AISI 316 stainless steel cylindrical reactor, 1 sq cm in cross section and 50 cm high, at a rate of approximately 29 N litres/hr.

The gaseous mixture was contacted in the reactor at a temperature of 266°C and a pressure of 1 atm with a catalyst in the form of balls of silver 3—4 mm in diameter on alumina as carrier, the silver content amounting to about 15%.

The conversion per pass was found to be approximately 6% with respect to the ethylene feed, with a selectivity in respect of ethylene amounting to 72—73% approximately with respect to the reacted ethylene.

EXAMPLE 2

A gaseous mixture of the composition: ethylene (99.7% purity) 94% by volume; oxygen (99.5% purity) 6% by volume was caused to flow at a rate of 31 N cubic metres/hour through a reactor comprising 3 AISI 316 stainless steel tubes 2.54 cm in diameter and 6 m in height. Traces of 1,1-dichloroethane were included in the gas feed as a reaction moderator.

The gaseous mixture was contacted in the reactor at a temperature of 280°C and a pressure of 12 atm with a catalyst in the form of 6 mm balls consisting of silver on an alumina carrier, the silver content of the catalyst being about 15%.

The gas issuing from the reactor was conveyed at 30°C and 12 atm through an absorption column containing packing in counter-current to water percolating from the top. The ethylene oxide was thus absorbed substantially completely by the water which was employed in a quantity so as to obtain an aqueous solution with a content of ethylene oxide of about 1.3%. This solution was passed to a stripper and stripped with steam; the rate of production of ethylene oxide from the stripper was approximately 1350 g/hr, with a selectivity with respect to ethylene of about 73%.

The gas issuing from the ethylene oxide scrubbing column was conveyed at 30°C and 12 atm through a second packed column countercurrently to an aqueous 8% sodium

hydroxide solution. This substantially completely removed the carbon dioxide from the gas. The gas was recycled to the oxidation reactor together with additional ethylene and oxygen as required to restore the composition of the reagents to the abovementioned values.

EXAMPLE 3

A further test was carried out utilizing the gaseous mixture as in Example 2 with a volumetric composition of: ethylene 94%; oxygen 6% in the same apparatus as described in Example 2 and under similar conditions.

The temperature of the reactor was again maintained at 280°C, but the pressure was increased to 18 atm. The rate of feed of the gaseous reagents was 47.6 N cu m/hr.

The rate of production of ethylene oxide was approximately 2,100 g/hr, with a selectivity with respect to ethylene of about 73.5%.

WHAT WE CLAIM IS:—

1. A process for preparing ethylene oxide by catalytic oxidation in the vapor phase at high temperature and a pressure of 1 to 30 atm. of ethylene with oxygen, wherein into an oxidation reactor containing an oxidation catalyst are introduced substantially pure ethylene and oxygen, separately and/or premixed, without gaseous diluents, the ethylene constituting more than 86% by volume with respect to the gases entering the reactor.

2. A process as claimed in claim 1, wherein the oxygen content in the mixture fed to the oxidation reactor amounts to from 4 to 6% by volume, the remainder being essentially ethylene.

3. A process as claimed in claim 1 or 2, wherein the oxidation catalyst is silver deposited on an inert support, the silver content of the catalyst amounting to from 5 to 20% by weight of the catalyst.

4. A process as claimed in any of the preceding claims, wherein the oxidation reactor is maintained at a temperature of from 150°C to 450°C.

5. A process as claimed in claim 4, wherein the temperature is 250°C to 320°C and the pressure is 10 to 20 atm.

6. A process as claimed in any of the preceding claims, wherein the residence time of the gaseous mixture in the oxidation reactor amounts to from 3 to 10 seconds.

7. A process as claimed in claim 5, wherein the residence time is 5 to 8 seconds.

8. A process as claimed in any of the preceding claims, wherein the gases issuing from the oxidation reactor are cooled to a temperature below about 130°C, and ethylene oxide is recovered therefrom by scrubbing with water or another solvent, the scrubbing being carried out at a pressure of from 1 to 30 atm and at a temperature of from 5 to 80°C.

9. A process as claimed in any of claims 1 to 7, wherein the gaseous reaction mixture from the oxidation reactor is cooled, passed to a first scrubbing column in which ethylene oxide is separated and then to a second column in which the carbon dioxide or other by-products of the oxidation reaction are separated, and the gases issuing from the second tower are recycled to the oxidation reactor after the gaseous mixture has been restored to the feed composition by adding fresh oxygen and ethylene thereto.

10. A process for preparing ethylene oxide, substantially as hereinbefore described with reference to any of the foregoing Examples.

11. Ethylene oxide when prepared by a process as claimed in any of the foregoing Examples.

H. D. FITZPATRICK & CO.,

Chartered Patent Agents,
27 Chancery Lane, London, W.C.2, and
14—18 Cadogan Street, Glasgow, C.2.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1970.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

BEST AVAILABLE COPY